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Test Report T66-3-1

DETERMINATION OF CARBON BLACK AND GRAPHITE IN NITROCELLULOSE-BASE
PROPELLANTS

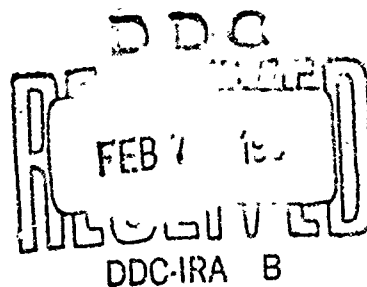
by

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DETERMINATION OF CARBON BLACK AND GRAPHITE IN NITROCELLULOSE-BASE
PROPELLANTS

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November 1965

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SUMMARY

The entire problem of determining carbon black and graphite in nitrocellulose-base propellants was investigated. It is shown that available methods for the determination of carbon black leave much to be desired, especially if carbon black and graphite are both present. A new spectrophotometric method for the determination of carbon black in propellants is proposed that depends upon the yellow color obtained when carbon black is dissolved by boiling with nitric acid. Channel blacks and smaller size furnace blacks (the usual carbon blacks found in nitrocellulose-base propellants) require 3 hours of boiling, while larger size furnace blacks and fine thermal blacks require 5 hours boiling. The color is due to polycarboxylic acids with cyclic nuclei. It is suggested that an absorptivity factor be established by the use of the same type of carbon black as was used in the propellant. The absorptivity factors obtained for different types of carbon blacks are tabulated. Before the development of the color, the carbon black is separated by dissolution of the propellant in morpholine and filtration through a sintered porcelain crucible containing an asbestos mat. The residue is washed with acetone, hot water, and hot hydrochloric acid. The range of the spectrophotometric method is 0 to 0.5%. Carbon black in the range of 0.15 to 10% can be determined gravimetrically after the morpholine separation. Graphite does not interfere with the spectrophotometric method for carbon black but does interfere with the gravimetric method. If both carbon black and graphite are to be determined, the total of carbon black and graphite is determined gravimetrically after the morpholine treatment, the carbon black is determined spectrophotometrically by treating the combined residue with nitric acid, and the graphite is calculated by difference. Improved gravimetric procedures are proposed for the determination of graphite in nitrocellulose-base propellants by the morpholine, nitric acid, and nitric-hydrochloric acid methods. Also described is an improved procedure for the determination of graphite and tin on the same sample. The results obtained for all the methods for graphite are compared.

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I. SUMMARY

The entire problem of determining carbon black and graphite in nitrocellulose-base propellants was investigated. It is shown that available methods for the determination of carbon black leave much to be desired, especially if carbon black and graphite are both present. A new spectrophotometric method for the determination of carbon black in propellants is proposed that depends upon the yellow color obtained when carbon black is dissolved by boiling with nitric acid. Channel blacks and smaller size furnace blacks (the usual carbon blacks found in nitrocellulose-base propellants) require 3 hours of boiling, while larger size furnace blacks and fine thermal blacks require 5 hours boiling. The color is due to polycarboxylic acids with cyclic nuclei. It is suggested that an absorptivity factor be established by the use of the same type of carbon black as was used in the propellant. The absorptivity factors obtained for different types of carbon blacks are tabulated. Before the development of the color, the carbon black is separated by dissolution of the propellant in morpholine and filtration through a sintered porcelain crucible containing an asbestos mat. The residue is washed with acetone, hot water, and hot hydrochloric acid. The range of the spectrophotometric method is 0 to 0.5%. Carbon black in the range of 0.15 to 10% can be determined gravimetrically after the morpholine separation. Graphite does not interfere with the spectrophotometric method for carbon black but does interfere with the gravimetric method. If both carbon black and graphite are to be determined, the total of carbon black and graphite is determined gravimetrically after the morpholine treatment, the carbon black is determined spectrophotometrically by treating the combined residue with nitric acid, and the graphite is calculated by difference. Improved gravimetric procedures are proposed for the determination of graphite in nitrocellulose-base propellants by the morpholine, nitric acid, and nitric-hydrochloric acid methods. Also described is an improved procedure for the determination of graphite and tin on the same sample. The results obtained for all the methods for graphite are compared.

II. RECOMMENDATIONS

It is recommended that the improved procedures for carbon black and graphite be incorporated into the military specification for propellants (MIL-STD-286A, Military Standard, Propellants, Solid: Sampling, Examination, and Testing).

III. INTRODUCTION

Carbon black is frequently added to propellants to improve the burning characteristics and decrease the heat radiation to the interior of the grain. Graphite is added to propellants to modify its burning characteristics or is applied as a glaze to act as a lubricant and prevent the accumulation of static electricity. Some propellants contain both carbon black and graphite.

The methods presently used for the determination of carbon black and graphite leave much to be desired. This is especially true for carbon black. This arsenal, therefore, undertook an investigation on the entire problem of determining carbon black and graphite in propellants with the view of developing improved procedures.

IV. STUDY

A. PREVIOUS METHODS FOR THE DETERMINATION OF CARBON BLACK AND GRAPHITE

1. Carbon Black

Carbon black in propellants has been determined by the following methods:

a. Digestion with concentrated nitric acid or 1 to 1 nitric acid at gentle heat, filtration through a Gooch crucible, washing with acetone (or a mixture of ether and acetone), drying at 120° to 130° C., weighing, heating at 600° to 650° C., and taking the loss in weight to be carbon black (15, 24).

b. Dissolution in sodium hydroxide solution and hydrogen peroxide, filtration, and proceeding as in a (19).

c. Dissolution in sulfuric acid and hydrogen peroxide, filtration, and proceeding as in a (20).

d. Spectrophotometrically by measurement of the black color (at 540 millimicrons) produced by the suspension of the carbon black when the propellant is dissolved in a mixture of acetone and acetic acid (16).

2. Graphite

Graphite in propellants has been determined by the following methods:

a. The same as method a for carbon black (15); however, the temperature for the nitric acid digestion is not critical (14).

b. The same as method b for carbon black (19).

c. The same as method c for carbon black (20).

d. Dissolution of the sample in morpholine, washing successively with water, 3N hydrochloric acid and ether, drying at 100° C., weighing, ignition at 600° to 650° C., and taking the loss in weight to be graphite (12).

e. Graphite and tin can be determined on the same sample by digesting with nitric acid, filtering off the graphite and metastannic acid by means of a Gooch crucible, drying at 350° C. to obtain the weight of graphite and tin dioxide, ignition at 800° C., calculation of the loss in weight as graphite, and calculation of the tin by difference (13).

3. Carbon Black and Graphite

The following methods have been used to determine carbon black and graphite when both are present in the propellant:

a. Dissolution in concentrated nitric acid, filtration by means of a Gooch crucible or sintered porcelain crucible containing an asbestos mat, drying at 120° to 130° C., weighing, treatment of the crucible and contents with nitric acid for 3 hours under a reflux condenser to dissolve the carbon black, filtration, drying at 120° to 130° C., calculation of the carbon black by loss in weight from the nitric acid treatment, and calculation of the graphite by loss in weight on heating at 600° to 650° C. (14).

b. Dissolution of the sample in 1 to 1 nitric acid, filtration, and determination of the total of carbon black and graphite by drying at 120° to 130° C., weighing, igniting at 600° to 650° C., and weighing again. A second sample is heated under reflux with 1 to 1 nitric acid for 3 hours to dissolve the carbon black, the solution is filtered, the graphite alone is determined, and the carbon black is calculated by difference (24).

B. ERRORS IN PREVIOUS METHODS FOR THE DETERMINATION OF CARBON BLACK AND GRAPHITE

The gravimetric methods for carbon black are subject to the following errors:

- a. Attack of the carbon black by the dissolution agent.
- b. Loss of carbon black as a colloid during the filtration.
- c. Contamination by materials that are not completely soluble in the dissolution agent or washing solution. Nitro-cellulose and tin are important interferences in this respect. It has been suggested that tin be held in solution by adding some hydrochloric acid with the nitric acid (15), but this increases the danger of dissolution of carbon black.

d. Change in weight of the asbestos between weighing due to volatilization of impurities in the asbestos.

The spectrophotometric (nephelometric) method for carbon black is subject to the following errors:

- a. The color is dependent on the particle size of the carbon black. To eliminate this error it is necessary to use the identical carbon black for the standard as is present in the sample (16).
- b. The other ingredients present in the propellant influence the color. It is recommended that the same ingredients be added to the standard as are present in the sample (16); however, the interference of graphite and certain other dark colored materials cannot be eliminated in this manner.

The methods for graphite are subject to the following errors:

- a. Contamination of the graphite by materials that are not completely soluble in the dissolution agent or washing solution.
- b. Change in weight of the asbestos between weighings, due to volatilization of impurities in the asbestos.
- c. Failure to burn off the graphite completely before making the second weighing.

d. Absorption of some oxygen or nitrate by the graphite, forming so called "graphitic oxide" or graphitic nitrate" (3).

e. Conversion of impurities in the graphite (such as iron and silicon) to solid oxides on igniting the graphite. This error would ordinarily be significant only if natural graphite were used in the propellant. The maximum permissible ash content of natural graphite used in propellants is 6%, while the maximum permissible ash content of artificial graphite used in propellants is 0.5% (5).

The methods for determining both carbon black and graphite are subject to the following errors:

a. In determining the total of the carbon black and graphite the same errors are encountered as in the determination of carbon black and graphite alone (attack of the carbon black, loss of carbon black as a colloid, contamination, change in weight of the asbestos, and absorption of oxygen or nitrate by the graphite).

b. In determining the carbon black by calculating the loss in weight caused by the dissolution of carbon black in nitric acid, an important error is the failure of the carbon black to dissolve completely after the 3-hour refluxing with nitric acid. As will be shown later, some types of carbon black will only partially dissolve after 3 hours boiling with nitric acid.

C. CHARACTERIZATION OF CARBON BLACKS

There is some confusion in the literature on what constitutes a carbon black. The most generally accepted designation is that carbon blacks include three classes of materials, namely, channel black, furnace black, and thermal black (9, 21, 22, 25). Lamp-black, acetylene black, charcoal, bone black, and graphite are generally not considered to be carbon blacks (9, 21, 22, 25).

To throw light on the characterization of carbon blacks, the methods used to manufacture the above materials will be considered briefly. Channel black is made by impinging a flame of burning natural gas against a cooler iron surface and scraping the deposited carbon. Furnace black is made by burning natural gas or vaporized aromatic hydrocarbon oil in a closed furnace with about 50% of the air required for complete combustion, followed by the separation of the carbon black by cooling with a water spray. The furnace black produced from natural gas is called gas furnace black while that produced from aromatic hydrocarbon oil is called oil furnace black. Thermal furnace black is made by thermal decomposition of

natural gas by passing it through a heated brick checkerboard network. Lampblack is made by burning oil in a free flame and collecting the carbon so produced away from the flame. Acetylene black is made by the thermal decomposition of acetylene. The decomposition of acetylene is exothermic in contrast to the decomposition of natural gas which is endothermic, consequently the properties of acetylene black and thermal black are quite different. Charcoal is made by the destructive distillation of vegetable substances such as wood. Bone black is made by the destructive distillation of bones. Artificial graphite is made by heating coke in an electric furnace at a very high temperature. Natural graphite is a mineral.

The above materials differ in their properties in many respects. One difference of importance to the present investigation is the percentage of carbon. The following are typical percentages of carbon: channel black, 85 to 95; furnace black, 99; thermal black 95 to 99.5; lampblack, 90 to 99; charcoal 50 to 95; bone black, 10 to 20 (the remainder is chiefly calcium phosphate); synthetic graphite 91 to 99; natural graphite, 78 to 92. The impurities present in carbon black are for the most part oxygen and moisture.

Another important difference between the above materials is particle size. The particle size ranges (millimicrons) of the following materials as produced commercially are: channel black, 8 to 30; furnace black, 18 to 80; lampblack, 65 to 100; acetylene black, 40 to 50. Thermal black is produced in two grades, namely fine thermal black which is about 160 to 190 millimicrons and medium thermal black which is about 450 to 500 millimicrons. Charcoal, bone black, and graphite are usually ground to a definite mesh size, such as 325 mesh.

There is a difference in surface area between the above materials. The finer the particle size, the greater the surface area. Charcoals have a very large surface area because of their porosity.

There is also a difference in structure. Graphite is a definitely crystalline material in which carbon atoms are arranged in sheets of regular hexagons. Carbon black, lampblack, acetylene black, and charcoals are microscopically crystalline in character and are made of crystallites with graphite structure oriented in random fashion (3, 8). Usually, the higher the temperature of formation of carbonaceous black, the greater will be the resemblance to the true graphite structure. For this reason acetylene black and thermal black have the greatest resemblance to graphite in structure while charcoals have the least resemblance.

The types of carbon blacks used in propellants include channel black, furnace black, and fine thermal black. Medium thermal black and acetylene black are not used in propellants. Lampblack is apparently not used in present day propellants; however, it was a common constituent of European propellants around 1890.

There are two limited coordination military specifications for carbon black used in Ordnance, namely MIL-C-00306A for carbon black used in rocket propellants (10) and MIL-C-11403 for carbon black used in "burning-type munitions" (11). A definite type of carbon black is not specified in MIL-C-00306A (channel black was specified in JAN-C-306(4) which MIL-C-00306A superseded). Furnace black is specified in MIL-C-11403.

D. STUDY OF THE COLOR PRODUCED BY THE REACTION OF CARBON BLACK AND NITRIC ACID

Reaction of Nitric Acid with Different Carbonaceous Materials

It was found that a yellow color was produced when carbon black was dissolved in nitric acid by prolonged boiling. It was decided to apply this color to the determination of carbon black in propellants.

Portions (5 to 25 mg) of samples of channel black of particle size 9, 10, 12, and 17 millimicrons were treated with 145 ml of nitric acid in covered 500-ml tall form beakers and the solutions were boiled down to a volume of 50 to 60 ml over a period of 3 hours. The solutions were diluted, filtered through Whatman No. 42 filter papers, cooled, and diluted to 250 ml. The colors were read at 400 millimicrons with a spectrophotometer set at 100% transmittance with the reagent blank. Straight line calibration curves were obtained.

The same experiment was repeated with samples of furnace blacks of 23, 26, 28, 42, 50, 70, 78, and 80 millimicrons, thermal black of 180 and 470 millimicrons, lampblack, acetylene black, wood charcoal, and bone black (50 to 200 mg portions of the last named material was used because of its low carbon content).

The charcoal and bone black dissolved in 2 hours and gave straight line calibration curves. The furnace black of particle size 23 to 50 millimicrons dissolved in 3 hours and also gave straight line calibration curves. The furnace black of 70 to 80 millimicrons, fine thermal black (180 millimicrons), and lampblack dissolved in 5 hours and likewise gave straight line calibration curves. The medium thermal black (470 millimicrons) and acetylene black were only about 25% attacked (as judged by filtering two

samples through a Gooch, drying, and weighing) at the end of 5 hours. Graphite was not attacked at all at the end of 5 hours and gave a colorless solution (after filtration) which showed no absorbance at 400 millimicrons.

A very slight black residue always remains after dissolution of carbon blacks in nitric acid even after heating for 5 hours. The residue is probably graphitic in nature (it has been noted that a small amount of graphite is found in carbon blacks (2,3)).

Why do some carbonaceous blacks dissolve more readily in nitric acid than do others? There are apparently three important factors involved, namely particle size, structure, and surface condition. The effect of particle size is readily seen from the fact that smaller size carbon blacks (all channel blacks and smaller diameter furnace black) dissolve in 3 hours. The blacks of medium particle size such as the larger size furnace black, fine thermal black (180 millimicrons), and lampblack require 5 hours of heating. Very large size blacks (thermal black of 470 millimicrons) do not dissolve even after 5 hours heating. The structure and surface condition of acetylene black helps to explain why this material is not dissolved after 5 hours heating, even though it has a relatively small particle size. The surface condition (porosity) of charcoal and bone black explains why these materials are dissolved in 2 hours.

The nitric acid that was used in all experiments for the spectrophotometric determination of carbon black was reagent grade concentrated nitric acid (70% HNO_3). This acid is a constant boiling mixture that does not change significantly in composition during prolonged boiling (although there is some decomposition to nitrogen dioxide, oxygen, and water) (7). The boiling point of concentrated nitric acid is 121°C .

During the initial boiling of the nitric acid with the carbon black, the color may seem more intense because of the nitrogen dioxide produced.

The color once developed is very stable and does not change on standing overnight.

Spectrophotometric Curve

The spectrophotometric curves (wave length vs. percent transmittance) obtained with different carbonaceous blacks seemed the same. The curve obtained for a sample of channel black over the range 400 to 700 millimicrons is shown in Figure 1. The curve confirms that 400 millimicrons is a satisfactory wave length for reading the color.

Calculation of Absorptivity Factor

The absorbance obtained will vary somewhat with the carbon black. A study was therefore made of the absorptivity factors obtained for different carbon blacks. We shall define the absorptivity factor as follows:

$$\text{absorptivity factor} = \frac{\text{absorbance}}{\text{mg of carbon black per 250 ml}}$$

Somewhat less absorbance was obtained when the carbon black was carried through the morpholine extraction procedure, than when the sample was treated directly with nitric acid and the solution filtered. It is possible that the morpholine (and acetone used as a wash) dissolves out some color-forming material. It is recommended, therefore, that the absorptivity factor be calculated by carrying the carbon black through the procedure.

The absorptivity factors for different carbon blacks, determined in duplicate, after first drying the samples at 105° C. for 2 hours, are shown in Table I. Also, shown are pertinent data on the various properties of the carbon blacks. The average absorptivity factors for the different types of carbon blacks were as follows: channel black (3 hour boiling), 0.0221; furnace black of 50 millimicrons and less (3 hour boiling), 0.0267; furnace black greater than 50 millimicrons (5 hour boiling), 0.0245; fine thermal black (5 hour boiling), 0.0150. If it is not possible to obtain a sample of the identical carbon black used in propellant a fairly reliable result could be obtained by using the above factors for the general type of carbon black.

The lower percentage of carbon in channel black (Table I) might explain the fact that this type of carbon black gives a lower absorptivity factor than furnace black.

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The lower percentage of carbon in channel black (Table I) might explain the fact that this type of carbon black gives a lower absorptivity factor than furnace black.

It was found necessary after the morpholine filtration, to wash the carbon black with acetone to remove residual nitrocellulose and other organic contaminants, then with hot water to remove soluble salts (nitrates, perchlorates, sulfates, etc.), and finally with hot hydrochloric acid to remove carbonates, organic lead salts, barium chromate, nitroguanidine, and other materials. Organic lead salts will cause slightly high results, if they are not removed while barium chromate will cause very high results. RDX and oxamide are not completely removed by the above washings but the amount that remains does not interfere with the carbon color.

After the treatment with nitric acid to develop the color, water is added and the solution is filtered through a filter paper. A filtering crucible should not be used for this filtration since the rubber adapter of the suction flask will be attacked by the nitric acid, producing an interfering color.

The recommended range for the spectrophotometric method is 0 to 0.5%.

Carbon black in the range 0.15 to 10% can be determined gravimetrically after the morpholine separation. The gravimetric method, of course, is not applicable in the presence of graphite. For the gravimetric method, the crucible and precipitate are washed with hot morpholine, acetone, hot water, hot hydrochloric acid, water, and acetone in that order. The hydrochloric acid wash must always be used when determining carbon black (or carbon black plus graphite) gravimetrically in order to ensure the dissolution of calcium carbonate. According to observations in this laboratory, calcium carbonate is frequently found in propellants.

If tin is present in the propellant and the determination for carbon black is to be performed gravimetrically, then hydrochloric acid containing a small amount of antimony trichloride (500 ml of hydrochloric acid and 0.1 gram of antimony trichloride) should be substituted for the hydrochloric acid. The antimony trichloride acts as a catalyst for the dissolution of the tin. Too much antimony trichloride will cause high results for carbon black because of the precipitation of metallic antimony.

RDX and oxamide will cause somewhat high results for the gravimetric determination of carbon black. Propellants containing RDX and oxamide would ordinarily contain less than 0.5% carbon black (hence, the determination could be run spectrophotometrically in any case).

If graphite and carbon black are both to be analyzed, the total of graphite and carbon black is determined gravimetrically after the morpholine separation, the combined residue is treated with nitric acid to develop the carbon color, and the graphite is calculated by difference. Propellants that contain both carbon black and graphite ordinarily do not contain more than 0.5% carbon black.

For both the spectrophotometric and gravimetric techniques, it is essential that the asbestos receive a prior treatment that consists of digesting with hydrochloric acid at about 95° C. for about 13 hours. This treatment dissolves impurities that would otherwise dissolve during the boiling with the nitric acid, causing erratic results for the spectrophotometric method from colored impurities in the asbestos. The treatment also dissolves impurities that would otherwise dissolve in the washing with hot hydrochloric acid, causing erratic results with gravimetric method.

A sintered porcelain crucible of fine porosity containing an asbestos pad is used for the filtration of the morpholine solution of the propellant. A Gooch crucible is not satisfactory since it will not retain fine carbon black. The filtering crucible containing the pad must be ignited at 800° C. for 40 minutes before it can be used. This ignition removes organic matter from the asbestos that may react with the nitric acid. Also, it removes particles of graphite that may have become imbedded in the pores of the frit during the boiling with nitric acid in a prior determination.

The spectrophotometric method is primarily designed for the determination of carbon black in nitrocellulose-base propellants. No recommendations are made concerning the possible application of the method to non-nitrocellulose types of propellants because of the varied nature of these propellants. Ordinarily, the use of morpholine as a solvent would offer no particular advantage in the analysis of non-nitrocellulose type propellants.

F. RECOMMENDED METHOD FOR THE DETERMINATION OF CARBON BLACK IN NITROCELLULOSE-BASE PROPELLANTS

Apparatus and Reagents

Spectrophotometer. A Beckman Model B spectrophotometer was used in this laboratory.

Coor No. 4A sintered porcelain crucible.

Treated asbestos. Add about 35 grams of a good grade of asbestos to a 1-liter beaker and add hydrochloric acid to within an inch of the top of the beaker. Place on a steam bath or the edge of the hot plate and heat at about 95° C. for 8 hours with occasional stirring. Decant and discard most of the hydrochloric acid, add a second portion of hydrochloric acid, and digest at about 95° C. for 5 more hours. Decant, add hot water, filter through a large Buchner funnel containing a Whatman No. 41H filter paper (to hold the fines), and wash thoroughly with hot water. Transfer to a bottle and add water.

Hydrochloric acid - antimony trichloride solution. Dissolve 0.1 gram of antimony trichloride in 500 ml of hydrochloric acid.

Spectrophotometric Procedure for Carbon Black (Less than 0.5%)

Prepare a filtering crucible by pouring a fairly thick suspension of asbestos in water into a Coor No. 4A crucible, applying suction until the water has drained, and then repeating the treatment with another portion of asbestos, so as to form a pad 1/4 inch thick. Wash with water and ignite in a muffle at 800° C. for 40 minutes.

Transfer 5 grams of the propellant to a 250-ml beaker and add 60 ml of morpholine. If the propellant is extremely finely divided, cool the morpholine in an ice bath before adding it in order to prevent a possible vigorous reaction. Cover with a watch glass, insert a stirring rod, and warm on an electric hot plate under a hood with occasional stirring until the sample is in solution (approximately 15 to 30 minutes). Heat to incipient boiling (white fumes will appear) and filter while hot through the filtering crucible (it is essential that the solution be filtered hot). Wash the beaker and crucible with hot morpholine, then wash well with acetone and hot water. Empty the suction flask and add about 200 ml of tap water (to act as a trap for hydrogen chloride in the next step). Wash with hot hydrochloric acid (temperature about 80° C.) poured from a beaker and then wash with hot water.

Detach the pad from the crucible with a sharp instrument, transfer the pad and crucible to a 500-ml tall form beaker (with a lip), and then wash down the end of the instrument with about 1 ml of water from a wash bottle. If the carbon black is furnace black of particle size of 50 millimicrons or less (the information on the particle size is furnished by the manufacturer) or any grade of channel black, add 145 ml of nitric acid. If the carbon black is furnace black of particle size greater than 50 millimicrons, or fine thermal black, add 170 ml of nitric acid. Cover with a tight-fitting watch glass, heat to boiling, and boil moderately for 3 hours

if 145 ml of nitric acid has been added, or 5 hours if 170 ml of nitric acid has been added. Swirl occasionally during the boiling. The volume at the end of the boiling period should be 50 to 70 ml. If the volume is greater than 80 ml at 1 hour before the end of the boiling period, remove the watch glass (there is no danger of loss because of the tall form beaker).

Dilute to about 175 ml with water, insert a stirring rod and filter through a Whatman No. 42 filter paper into a 250-ml volumetric flask. Wash the crucible, beaker, and filter paper with 1 to 9 nitric acid.

Measure the absorbance at 400 millimicrons with a spectrophotometer that has been set to 100% transmittance with water.

Determine the absorptivity factor for the type of carbon black present in the propellant by drying a sample of the carbon black at 105° C., weighing out a 12 to 16 mg portion to 0.1 mg (using the catch weight technique), and carrying the sample through the entire procedure.

Calculate the absorptivity factor from the standard as follows:

$$\text{absorptivity factor} = \frac{\text{absorbance of standard}}{\text{mg of carbon black in 250 ml}}$$

Calculate the percent carbon black in the propellant as follows:

$$\% \text{ carbon black} = \frac{\text{absorbance of sample}}{\text{absorptivity factor} \times \text{grams of sample} \times 10}$$

Notes:

To clean the crucibles, fill them with water and rub the bottoms with a stiff brush made by cutting the bristles of a lettering brush (1/4 inch diameter) so that the length of the bristles are 1/4 inch.

Do not heat the crucibles over an open flame, since such treatment may cause them to crack.

Gravimetric Procedure for Carbon Black (0.15 to 10%)

Prepare a sintered crucible with an asbestos mat as described above, but after the ignition at 800° C. cool in a desiccator and weigh. Use a 5-gram sample for 0.15 to 1% carbon black and a 2-gram sample for 1 to 10% carbon black. Proceed with the dissolution in

morpholine and filtration as described above. Wash with hot morpholine, acetone, hot water, and hot hydrochloric acid as described above. If tin is present, substitute the following treatment for the hydrochloric acid wash. Fill the crucible with hydrochloric acid-antimony trichloride solution (that has just previously been heated to an incipient boil) and allow to stand for several minutes without suction until the effervescence ceases. Repeat this treatment twice more.

Finally wash the crucible with water and then with acetone. Allow the acetone to drain off completely, dry at 200° C. for 40 minutes, cool in a desiccator, and weigh.

Calculate as follows:

$$\% \text{ carbon black} = \frac{\text{grams of precipitate}}{\text{grams of sample}} \times 100$$

Procedure When Both Carbon Black and Graphite Are To Be Determined

Proceed as in the gravimetric method for carbon black. After drying at 200° C., weigh the combined carbon black and graphite, and calculate the total percent of carbon black plus graphite. Transfer the asbestos pad and crucible to the 500-ml beaker, treat with nitric acid, develop the color as described, and calculate the percent carbon black. Calculate the percent graphite by deducting the percent carbon black from the total percent of carbon black plus graphite.

G. RESULTS FOR CARBON BLACK (AND CARBON BLACK AND GRAPHITE) IN NITROCELLULOSE-BASE PROPELLANTS

The results obtained for carbon black (and carbon black and graphite) on three actual propellants are shown in Table II. The first sample, which contained about 0.2% carbon black and no graphite, was analyzed for carbon black by both the spectrophotometric and gravimetric methods. The other two samples contained both carbon black and graphite. The results obtained for carbon black spectrophotometrically in the first sample checked the results obtained gravimetrically. All results showed good precision.

The recoveries obtained for carbon black on synthetic samples using the spectrophotometric method are shown in Table III. The recoveries obtained for carbon black and graphite on synthetic samples using the spectrophotometric method are shown in Table IV. The recoveries in both cases were satisfactory.

The recoveries obtained for carbon black by the gravimetric method are shown in Table V. These recoveries were also satisfactory.

H. DETERMINATION OF GRAPHITE BY MORPHOLINE METHOD

The gravimetric morpholine method for graphite is the same as the gravimetric morpholine method for carbon black, except that a Gooch crucible can be used in place of the sintered porcelain crucible with an asbestos pad.

I. DETERMINATION OF GRAPHITE BY NITRIC ACID AND NITRIC-HYDROCHLORIC ACID METHODS

Some methods for the determination of graphite in propellants by the nitric acid method specify a 10-gram sample (14, 24). The use of this large size sample was found to cause erratic results, because of the large amount of nitrocellulose that must be dissolved. The filtration was also slow. The use of a 5-gram sample (15) is advisable.

It is recommended that the sample be dissolved by treatment with 75 ml of nitric acid at about 90° to 100° C., followed by the addition of 30 ml of water and boiling for 10 minutes to drive off the oxides of nitrogen. The dilution with 30 ml of water prevents possible attack of the graphite and permits the solution to be filtered while hot.

If tin is present in the sample, it is recommended that 15 ml of hydrochloric acid and 60 ml of nitric acid be used for dissolving the sample. The hydrochloric acid should be added first, since metastannic acid, once precipitated, does not readily dissolve in hydrochloric acid.

Consideration was given to the desirability of eliminating the nitric acid method and using the nitric-hydrochloric acid attack for all samples. It was decided not to do this, however, since the nitric-hydrochloric acid method requires about 15 minutes more for dissolution of the sample than does the nitric acid method. Also, the nascent chlorine and nitrosyl chloride generated by the mixed acids makes the nitric-hydrochloric acid method somewhat more troublesome to work with.

It is recommended that the temperature for drying the graphite be 200° C. and the temperature for ignition of the graphite be 800° C. An ignition temperature of 600 to 650° C. which is used in one method for graphite (12) is definitely unsatisfactory.

The recommended nitric and nitric-hydrochloric acid methods for the determination of graphite are as follows:

Prepare a Gooch using the specially treated asbestos. Wash the Gooch with water and heat it in a muffle at 800° C. for 40 minutes.

Transfer a 5-gram sample to a 250-ml beaker. If tin is present, add 15 ml of hydrochloric acid and 60 ml of nitric acid; otherwise add 75 ml of nitric acid. Cover with a tight-fitting watch glass and heat at about 90° to 100° C. until the sample is in solution (30 to 45 minutes). Add 30 ml of water and boil for 10 minutes. Filter while hot through the Gooch crucible and transfer and wash with hot water. Discard the filtrate (Caution: nitric acid will produce a violent reaction with acetone to be used in the next step). Wash thoroughly with acetone. Allow the acetone to drain off completely. Dry at 200° C. for 40 minutes, cool in a desiccator, and weigh. Ignite in a muffle at 800° C. for 1 hour, cool in a desiccator, and weigh.

Calculate as follows:

$$\% \text{ graphite} = \frac{\text{loss in weight of crucible, grams}}{\text{grams of sample}} \times 100$$

J. DETERMINATION OF GRAPHITE AND TIN TOGETHER BY NITRIC ACID METHOD

As was noted at the beginning of this report, it is frequently customary to determine graphite and tin on the same sample after dissolving the propellant in nitric acid. However, the results for tin by this method may at times be very low. This was noted by John R. Ness of the du Pont Company and confirmed by this laboratory. The cause of the difficulty as traced in this laboratory was due to failure to boil the solution to precipitate the metastannic acid (several minutes of boiling are required). The directions in MIL-STD-286A(13) do not specify boiling. They state "allow the solution to simmer until the propellant is completely decomposed and the solution is reduced to 10 ml". The word "simmer", as defined by the dictionary, means "to be on the point of boiling". If this is the interpretation taken, then the results for tin will be very low, since vigorous boiling is essential. The tin is precipitated as metastannic acid on boiling in either a concentrated or dilute nitric acid solution. It is recommended that the propellant be dissolved in concentrated nitric acid by digesting at 90° to 100° C. and that water then be added and the solution boiled vigorously for 15 minutes.

The modified nitric acid method for the determination of graphite and tin is as follows:

Prepare a Gooch crucible with a fairly thick pad, using the specially treated asbestos. Ignite at 800° C. in a muffle for 40 minutes, cool in a desiccator, and weigh.

Transfer a 5-gram sample to a 250-ml beaker, add 40 ml of nitric acid, and cover with a tight fitting watch glass. Heat at about 90° to 100° C. until the sample is in solution (about 1 hour). Add 20 ml of water, heat to boiling, and boil vigorously for 15 minutes with the watch glass in place. Filter while hot through the Gooch crucible and transfer and wash with hot water. Discard the filtrate (Caution: nitric acid will cause a violet reaction with acetone to be used in the next step). Wash thoroughly with acetone and allow the acetone to drain off completely. Dry at 350° C. in a muffle for 40 minutes, cool in a desiccator, and weigh. Ignite at 800° C. in a muffle for 1 hour, cool in a desiccator, and weigh.

Calculate as follows:

$$\% \text{ tin} = \frac{78.77 (C-A)}{W}$$

$$\% \text{ graphite} = \frac{100 (B-C)}{W}$$

where A = weight of crucible, grams.

B = weight of crucible plus precipitate after heating at 350° C., grams.

C = weight of crucible plus precipitate after heating at 800° C., grams.

W = grams of sample.

K. RESULTS FOR GRAPHITE BY MORPHOLINE, NITRIC ACID, NITRIC-HYDROCHLORIC ACID, AND COMBINED GRAPHITE-TIN METHODS,
AND RESULTS FOR TIN BY GRAPHITE-TIN METHOD

The results obtained for graphite in three propellants by the morpholine, nitric acid, nitric-hydrochloric acid, and combined graphite-tin methods are shown in Table VI. The methods checked each other reasonably well. The recoveries obtained for graphite in synthetic samples, using the morpholine and nitric acid methods are shown in Tables VII and VIII, respectively. The morpholine method seems to give somewhat better recoveries than the nitric acid method.

On the basis of all the results for graphite it can be concluded that all the methods described for graphite are satisfactory. The choice of a method for a particular sample is a question of judgement. The nitric acid method is probably the most convenient and most reasonable method for the usual sample. When tin is present one of the other three methods must be used. It will be recalled that the morpholine method is not applicable to samples containing RDX or oxamide.

The results for tin by the combined graphite-tin method are shown in Table IX. Also shown are the results obtained for tin by the umpire volumetric method using granulated lead as the reducing agent and potassium iodate as the titrant (1, 17, 18). The results for tin by the combined graphite-tin method averaged 0.065% lower than the results for tin by the umpire volumetric method. This amounts to an error of -9.2% which would be acceptable only for very routine control work. It might be desirable to multiply the result obtained for tin by the empirical factor 1.1.

V. ACKNOWLEDGMENTS

The authors are indebted to Samuel Sitelman of this laboratory and John R. Ness of the du Pont Company, Penns Grove, New Jersey for their suggestions. Thanks are also expressed to Mr. Ness for furnishing samples of propellants and to Cabot Corporation, Huber Corporation, and Columbian Carbon Company for furnishing samples of carbon black.

VI. BIBLIOGRAPHY

- (1) Am. Soc. for Testing Materials, "1964 Book of ASTM Standards", Part 32, p. 375, Philadelphia, Pa., 1963.
- (2) Ellis, C., "Printing Inks", p. 176, Reinhold, New York, 1940.
- (3) Ephraim, F., "Inorganic Chemistry", Edited by Thorne, P. C. L., and Roberts, E. R., pp. 156, 157, Interscience, New York, 1954.
- (4) Joint Army-Navy Specification JAN-C-306, Carbon Black, Dry (for Use in Explosives), Jan. 1947.
- (5) Joint Army-Navy Specification, JAN-G-155, Graphite (for Use in Ammunition), June 1954.
- (6) Krevelen, D. W. Van, and Schuyer, J., "Coal Science", pp. 204, 205, Elsevier, New York, 1957.
- (7) McAlpine, R. K., and Soule, B. A., "Qualitative Chemical Analysis", p. 473, Van Nostrand, New York, 1933.
- (8) Mark, H. F., McKetta, J. J., and Othmer, D. F., "Encyclopedia of Chemical Technology", Vol. 4, p. 243, Interscience, New York, 1964.
- (9) Mattiello, J. J., "Protective and Decorative Coatings", Vol. 2, pp. 483 to 537, Wiley, New York, 1942.
- (10) Military Specification MIL-C-00306A, Carbon Black, Dry (for Use in Explosives), Nov. 1963.
- (11) Military Specification MIL-C-11403, Carbon Black, Dry (for Use in Munitions), July 1953.
- (12) Military Standard, MIL-STD-286A, "Military Standard Propellants, Solid: Sampling, Examination, and Testing", Jan. 1963, Method 305.1.1.
- (13) Ibid., Method 306.2.2.
- (14) Ibid., Method 308.1.3.
- (15) Ibid., Method 309.1.2.

VII. TABLES

Table I. Absorptivity Factors for Carbon Blacks

Carbon Black	Absorptivity Factor	Time of Boiling (hr)	Type of Carbon Black	Particle Size (Milli-microns)	Surface Area (sq. m./g.)	Fixed Carbon (%) ^a	Moisture (%) ^b	Ash (%) ^b	Volatile Matter (%) ^a	Benzene Extractable Matter (%) ^a
Carbolac 1	0.0217, 0.0209 Ave. 0.0213	3	Channel	9	950	84.0	6.37	0.03	16.0	0.0
R. Spectra	0.0224, 0.0228 Ave. 0.0226	3	Channel	10	1700	84.4	3.52	-----	15.6	0.0
Carbolac 2	0.0224, 0.0221 Ave. 0.0223	3	Channel	12	850	87.0	3.39	-----	13.0	0.0
Monarch 74	0.0224, 0.0218 Ave. 0.0221	3	Channel	17	320	95.0	1.51	-----	5.0	0.0
Huber-ISA	0.0265, 0.0255 Ave. 0.0260	3	Furnace	Beads	115	-----	1.58	-----	<1.0	-----
Regal 300R	0.0259, 0.0266 Ave. 0.0263	3	Furnace	Pluffy	84	99.0	0.53	-----	<1.0	0.10
Huber-BAP	0.0259, 0.0264 Ave. 0.0262	3	Furnace	Beads	78	-----	2.35	-----	<1.0	-----
Huber-FEY	0.0282, 0.0299 Ave. 0.0292	3	Furnace	Beads	42	-----	0.45	-----	<1.0	-----
Huber-GPY	0.0254, 0.0260 Ave. 0.0257	3	Furnace	Beads	50	-----	0.35	0.20	<1.0	-----
Molacco H	0.0246, 0.0253 Ave. 0.0250	5	Furnace	Pluffy	70	99.4	0.26	-----	0.6	-----
Huber-SRP	0.0220, 0.0230 Ave. 0.0225	5	Furnace	Beads	78	-----	0.15	-----	<1.0	-----
Sterling R	0.0252, 0.0265 Ave. 0.0259	5	Furnace	Pluffy	80	99.0	0.10	0.35	1.0	0.10
Sterling FT	0.0146, 0.0151, 0.0153 Ave. 0.0150	5	Fine Thermal	Pluffy	160	99.5	0.11	0.02	0.5	1.75

^a Manufacturer's analysis.

^b Analysis performed in this laboratory

- (16) Ibid., Method 309.2.2.
- (17) Military Standard MIL-STD-286A, "Military Standard Propellants, Solid: Sampling, Examination, and Testing", Change Notice 6, to be issued shortly.
- (18) Ness, J. R., du Pont Co., Penna Grove, N. J., written communication to Picatinny Arsenal.
- (19) Parpaillon, M., Mem. poudres, 34, 419 (1952).
- (20) Parpaillon, M., and Rigal, S., Mem. poudres, 42, 285 (1960).
- (21) Payne, H. F., "Organic Coating Technology", Vol. 2, pp. 906 to 923, Wiley, New York, 1961.
- (22) Rose, A., and Rose, E., "Condensed Chemical Dictionary", pp. 12, 218, 248, 521, 650, 1131, Reinhold, New York, 1956.
- (23) Ruof, C. H., Entel, J., and Howard, H. C., Fuel, 35, 409 (1956).
- (24) Welcher, F. J., "Standard Methods of Chemical Analysis", Vol. 2B, pp. 1378, 1385, Van Nostrand, New York, 1963.
- (25) Whitby, G. S., "Synthetic Rubber", pp. 399 to 403, Wiley, New York, 1954.

Table III. Results for Carbon Black in Synthetic Samples of Propellants

Sample	Carbon Black	
	Added (%)	Found (%)
5 g. DM ^a	0.05 (M74)	0.04
5 g. DM	0.06 (M74)	0.05
5 g. DM	0.13 (M74)	0.11
5 g. DM	0.24 (H-GPF)	0.26
5 g. DM	0.23 (RS)	0.23
5 g. DM	0.26 (RS)	0.26
5 g. DM	0.25 (H-GPF)	0.27
5 g. DM	0.38 (M74)	0.38
5 g. DM	0.50 (M74)	0.47
5 g. DM ^b	0.24 (H-GPF)	0.23
5 g. DM + 0.25 g. Pb Stearate	0.26 (H-GPF)	0.27
5 g. DM + 0.25 g. Pb Stearate	0.27 (STF)	0.27
5 g. DM + 0.25 g. Pb Stearate	0.25 (H-GPF)	0.28
5 g. DM + 2 g. nitroguanidine	0.25 (H-GPF)	0.27
5 g. DM + 2 g. nitroguanidine	0.24 (H-GPF)	0.25
5 g. A-1-Sn ^c + 2 g. nitroguanidine	0.46 (C-1)	0.49
5 g. DM + 0.05 g. Sn	0.25 (H-GPF)	0.24
5 g. DM + 0.05 g. Sn	0.22 (RS)	0.22
5 g. DM + 0.05 g. Sn	0.32 (H-FEF)	0.34
5 g. DM + 0.15 g. Pb ₃ O ₄	0.25 (STF)	0.24
5 g. DM + 0.15 g. Pb ₃ O ₄	0.25 (H-GPF)	0.23
5 g. DM + 0.15 g. Pb ₃ O ₄	0.22 (RS)	0.23
5 g. DM + 0.05 g. sulfur	0.24 (H-GPF)	0.25
5 g. DM + 0.05 g. sulfur	0.22 (STF)	0.24
5 g. DM + 0.15 g. PbCrO ₄	0.25 (RS)	0.23
5 g. DM + 0.15 g. PbCrO ₄	0.34 (H-FEF)	0.37
5 g. DM + 0.2 g. oxamide	0.24 (RH)	0.23
5 g. DM + 0.2 g. oxamide	0.25 (H-GPF)	0.25
5 g. DM + 0.2 g. oxamide	0.27 (RS)	0.26
5 g. DM + 0.2 g. RDX	0.23 (RH)	0.24
5 g. DM + 0.2 g. RDX	0.24 (H-GPF)	0.25
5 g. DM + 0.2 g. RDX	0.26 (H-GPF)	0.28

^a Contains (%): 90.3 nitrocellulose, 8.0 dinitrocoluene, 0.7 diphenylamine, 1.0 potassium sulfate.
^b Contains (%): 76.7 nitrocellulose, 19.42 nitroglycerin, 1.53 ethyl centralite, 1.45 calcium carbonate, 0.92 potassium nitrate.
^c Contains (%): 92.9 nitrocellulose, 5.55 dinitrocoluene, 0.79 diphenylamine, 0.76 potassium sulfate.

Table II. Results for Carbon Black and Graphite in Actual Samples of Propellants Using the Spectrophotometric Method

<u>Sample</u>	<u>Carbon Black Found Spectrophotometrically (%)</u>		<u>Carbon Black Found Gravimetrically</u>		<u>Graphite Found (%)</u>	
	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
8239a, b	0.21		0.18		0.24	
	0.18		0.19		0.23	
	0.21		0.18		0.23	
	0.18		0.20		0.22	
	0.18		0.18		0.24	
	<u>0.19</u>		<u>0.17</u>		<u>0.24</u>	
	0.19		0.18		0.23	
	0.015		0.011		0.009	
3238a, c						
	0.17				0.24	
	0.17				0.23	
	0.13				0.23	
	0.16				0.22	
	0.17				0.24	
	<u>0.18</u>				<u>0.24</u>	
	0.17				0.23	
	7.011				0.009	
3241a, d						
	0.08				0.10	
	0.10				0.09	
	0.10				0.08	
	0.10				0.10	
	<u>0.11</u>				<u>0.08</u>	
	0.10				0.09	
	0.311				0.013	

- a Carbon black present was Spheron 6 (a channel black).
b Contains (%): 92.7 nitrocellulose, 5.7 dinitrotoluene, 0.65 diphenylamine, 0.93 potassium sulfate.
c Contains (%): 92.5 nitrocellulose, 5.7 dinitrotoluene, 0.65 diphenylamine, 0.92 potassium sulfate.
d Contains (%): 87.9 nitrocellulose, 0.94 dinitrotoluene, 0.88 potassium sulfate, 0.75 tin.

Table V. Results for Carbon Black in Synthetic Samples by Gravimetric Morpholine Method

<u>Sample</u>	<u>Carbon Black Added (%)</u>	<u>Carbon Black Found (%)</u>
-----	0.16 (RS)	0.17
-----	0.40 (C-1)	0.39
-----	0.76 (RS)	0.78
-----	1.02 (C-1)	1.01
-----	1.02 (M74)	1.03
-----	1.04 (MH)	1.03
-----	1.00 (C-1)	1.02
5 g. OCK ^a	0.99 (M74)	1.03
5 g. OCK	1.01 (C-1)	0.99
5 g. OCK + 0.15 g. PbCrO ₄	1.00 (M74)	1.01
5 g. OCK + 0.15 g. PbCrO ₄	1.20 (C-1)	1.17
3 g. nitrocellulose + 0.4 g. KClO ₄ + 0.05 g. ethyl centralite	1.20 (M74)	1.21

^a Contains (%): 57.2 nitrocellulose, 25.1 nitroglycerin, 1.7 2-nitrodiphenylamine, 9.4 triacetin, 3.3 dioctylphthalate, 3.3 lead stearate.

Table IV. Results for Carbon Black and Graphite in Synthetic Samples of Propellants

Sample	Carbon Black	Graphite	Carbon Black	Graphite
	Added (%)	Present (%) ^a	Found (%)	Found (%)
5 g. DMR	0.24 (RS)	0.19	0.24	0.22
5 g. DMR	0.26 (RS)	0.19	0.26	0.20
5 g. DMR	0.25 (RS)	0.19	0.28	0.21
5 g. DMR	0.23 (H-ISAF)	0.19	0.23	0.19
5 g. DMR	0.23 (C-2)	0.19	0.20	0.16
5 g. DMR	0.24 (H-ISAF)	0.19	0.24	0.17
5 g. DMR	0.48 (H-ISAF)	0.19	0.50	0.13
5 g. DMR + 0.25 g. Pb Stearate	0.24 (H-GPF)	0.19	0.23	0.22
5 g. A-1-Sn + 0.25 g. Pb Stearate	0.49 (C-1)	0.25	0.51	0.25
5 g. DMR + 2 g. nitroguanidine	0.24 (RS)	0.19	0.25	0.22
5 g. DMR + 2 g. nitroguanidine	0.25 (H-GPF)	0.19	0.24	0.20
5 g. DMR + 2 g. nitroguanidine	0.31 (H-FEF)	0.19	0.28	0.21
5 g. DMR + 0.05 g. Sn	0.24 (MH)	0.19	0.23	0.16
5 g. DMR + 0.05 g. Sn	0.24 (RS)	0.19	0.24	0.23
5 g. DMR + 0.15 g. Pb ₃ O ₄	0.15 (STFF)	0.19	0.17	0.16
5 g. A-1-Sn + 0.15 g. Pb ₃ O ₄	0.46 (C-1)	0.23	0.49	0.26
5 g. DMR + 0.05 g. sulfur	0.22 (MH)	0.19	0.22	0.20
5 g. DMR + 0.05 g. sulfur	0.52 (RS)	0.19	0.52	0.17
5 g. DMR + 0.15 g. PbCrO ₄	0.26 (GTF)	0.19	0.24	0.22
5 g. DMR + 0.15 g. PbCrO ₄	0.24 (C-2)	0.19	0.26	0.20

^a Average of results by three methods (see Table VI).

Table VIII. Results for Graphite in Synthetic Samples by Nitric Acid Method

<u>Sample</u>	<u>Graphite Added (%)</u>	<u>Graphite Found (%)</u>
-----	0.29	0.31
-----	0.53	0.55
-----	1.00	1.02
5 g. nitrocellulose	0.25	0.27
5 g. nitrocellulose	0.50	0.54
5 g. nitrocellulose	0.97	0.98

Table IX. Results for Tin by Combined Graphite-Tin Method

<u>Sample</u>	<u>Tin Found by Graphite-Tin Method (%)</u>	<u>Tin Found by Umpire Volumetric Method (%)</u>
29		
A-1-Sn	0.60	0.66
	0.59	0.67
	0.57	0.66
	0.63	0.66
	0.59	0.66
	<u>0.59</u>	
	Ave. 0.60	Ave. 0.66
	Std. Dev. 0.021	Std. Dev. 0.005
T-2-Sn	0.71	0.75
	0.63	0.76
	0.60	0.76
	0.73	0.75
	0.73	0.75
	<u>0.70</u>	
	Ave. 0.68	Ave. 0.75
	Std. Dev. 0.055	Std. Dev. 0.007

Table VI. Results for Graphite in Propellants by Morpholine, Nitric Acid, Nitric-Hydrochloric Acid, and Combined Graphite-Tin Methods

Sample ID#	Morpholine		Nitric Acid		Nitric-Hydrochloric		Graphite-Tin		Ave. of All Methods (%)
	Method (%)		Method (%)		Method (%)		Method (%)		
A-1-Sn	0.22		0.20		0.19		-----		0.23
	0.21		0.21		0.16				
	0.22		0.19		0.20				
	0.20		0.16		0.21				
	0.21		0.16		0.20				
	0.21		0.16		0.19				
T-2-Sn	Ave. 0.21		Ave. 0.18		Ave. 0.19				0.19
	Std. Dev. 0.008		Std. Dev. 0.023		Std. Dev. 0.017				
	0.22		-----		0.28		0.23		
	0.22				0.27		0.24		
	0.23				0.23		0.23		
	0.22				0.22		0.23		
T-2-Sn	0.21				0.24		0.23		0.19
					0.23		0.22		
	Ave. 0.22				Ave. 0.25		Ave. 0.23		
	Std. Dev. 0.007				Std. Dev. 0.027		Std. Dev. 0.006		
	0.21		-----		0.21		0.18		
	0.19				0.20		0.18		
T-2-Sn	0.19				0.20		0.19		0.19
	0.20				0.20		0.17		
	0.19				0.19		0.17		
	0.21				0.20		0.17		
	Ave. 0.20				Ave. 0.20		Ave. 0.18		
	Std. Dev. 0.010				Std. Dev. 0.007		Std. Dev. 0.009		

Table VII. Results for Graphite in Synthetic Samples by Gravimetric Morpholine Method

Sample	Graphite Added (%)	Graphite Found (%)
5 g. nitrocellulose + 0.15 g. Pb stearate	0.32	0.33
5 g. nitrocellulose + 0.15 g. Pb stearate	0.49	0.50
5 g. nitrocellulose + 0.05 g. Sn	1.02	1.02

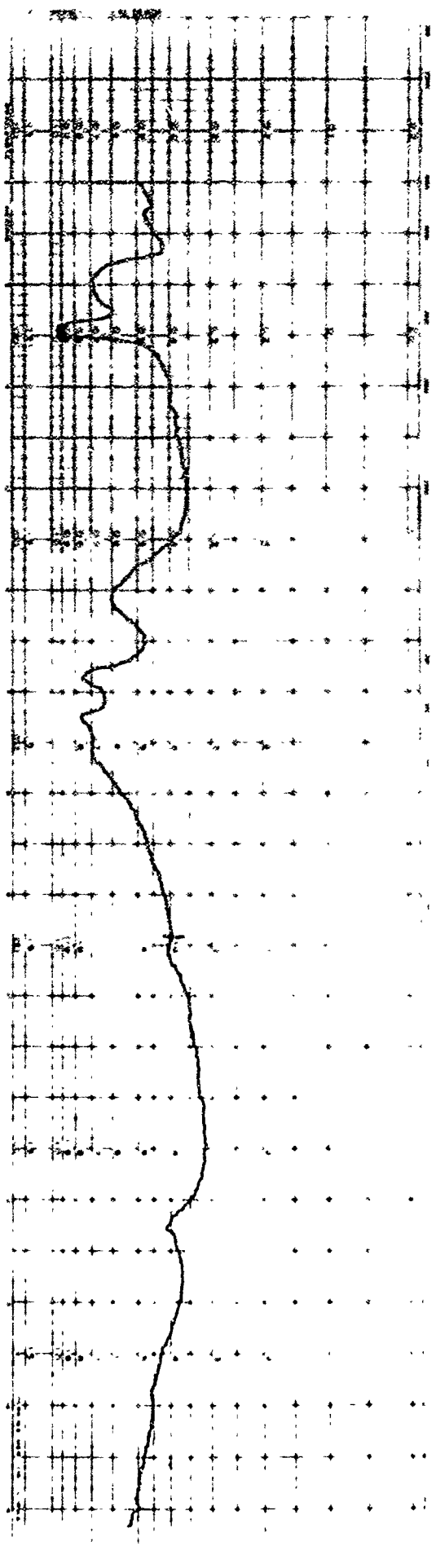
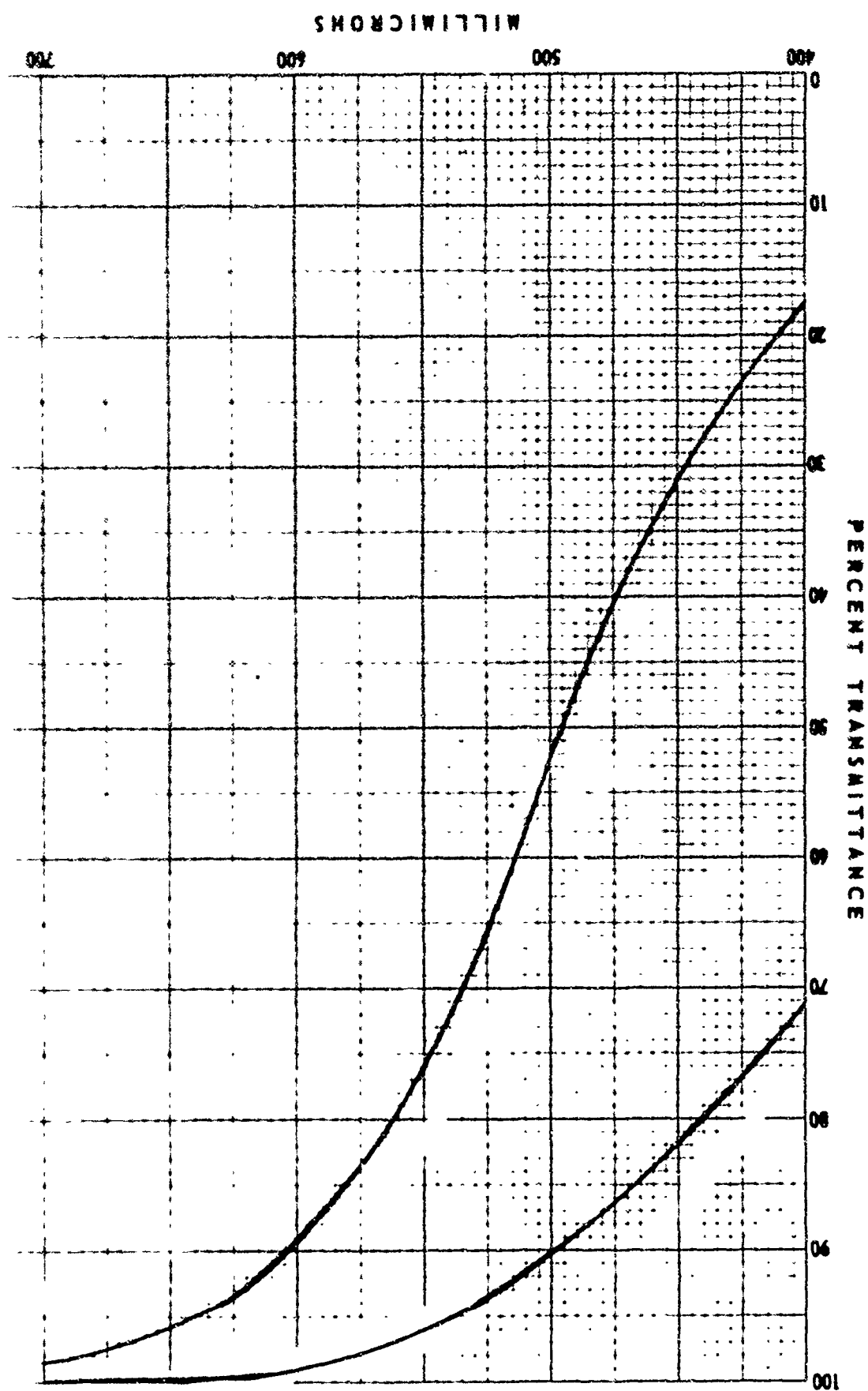


Figure 2. Infrared Spectrum of Colored Complex

Figure 1. Spectrophotometric Curve of Colored Complex



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13 ABSTRACT The entire problem of determining carbon black and graphite in nitro-cellulose-base propellants was investigated. It is shown that available methods for the determination of carbon black leave much to be desired, especially if carbon black and graphite are both present. A new spectrophotometric method for the determination of carbon black in propellants is proposed that depends upon the yellow color obtained when carbon black is dissolved by boiling with nitric acid. Channel blacks and smaller size furnace blacks (the usual carbon blacks found in nitro-cellulose-base propellants) require 3 hours of boiling, while larger size furnace blacks and fine thermal blacks require 5 hours boiling. The color is due to polycarboxylic acids with cyclic nuclei. It is suggested that an absorptivity factor be established by the use of the same type of carbon black as was used in the propellant. The absorptivity factors obtained for different types of carbon blacks are tabulated. Before the development of the color, the carbon black is separated by dissolution of the propellant in morpholine and filtration through a sintered porcelain crucible containing an asbestos mat. The residue is washed with acetone, hot water, and hot hydrochloric acid. The range of the spectrophotometric method is 0 to 0.5%. Carbon black in the range of 0.15 to 10% can be determined gravimetrically after the morpholine separation. Graphite does not interfere with the spectrophotometric method for carbon black but does interfere with the gravimetric method. If both carbon black and graphite are to be determined, the total of carbon black and graphite is determined gravimetrically after the morpholine treatment, the carbon black is determined spectrophotometrically by treating the combined residue with nitric acid, and the graphite is calculated by difference. Improved gravimetric procedures are proposed for the determination of graphite in nitrocellulose-base propellants by the morpholine, nitric acid, and nitric-hydrochloric acid methods. Also described in an improved procedure for the determination of graphite and tin on the sample sample. The results obtained for all the methods for graphite are compared.			

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